

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁷ : C08G 18/67, 63/91</p>	<p>A1</p>	<p>(11) International Publication Number: WO 00/64959 (43) International Publication Date: 2 November 2000 (02.11.00)</p>
<p>(21) International Application Number: PCT/EP00/03746 (22) International Filing Date: 19 April 2000 (19.04.00) (30) Priority Data: 99201294.8 26 April 1999 (26.04.99) EP (71) Applicant (for all designated States except US): AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL). (72) Inventor; and (75) Inventor/Applicant (for US only): VAN DIJK, Joseph, Theodorus, Maria [NL/NL]; Lage Morsweg 19, NL-2332 XA Leiden (NL). (74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Intellectual Property Department (Dept. AIP), P.O. Box 9300, NL-6800 SB Arnhem (NL).</p>		<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>
<p>(54) Title: COMPOSITION COMPRISING MERCAPTO-FUNCTIONAL COMPOUNDS</p> <p>(57) Abstract</p> <p>The present invention relates to a composition comprising: a compound comprising two or more olefinically unsaturated groups comprising at least one electron-withdrawing functionality linked to a carbon atom of the unsaturated bond; a compound comprising at least two mercapto-functional groups; and a catalyst comprising at least one, optionally blocked, NH-group. The invention further relates to a method for the application of the composition and to the use of the composition as a coating composition or an adhesive.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TC	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

COMPOSITION COMPRISING MERCAPTO-FUNCTIONAL COMPOUNDS

- 5 The present invention relates to a composition comprising:
- a compound comprising two or more olefinically unsaturated groups comprising at least one electron-withdrawing functionality linked to a carbon atom of the unsaturated bond;
 - a compound comprising at least two mercapto-functional groups; and
 - 10 - a catalyst.

Unsaturated groups, such as acryloyl groups, can react with active hydrogen-containing compounds. Such a reaction is believed to involve an addition of an anion derived from the nucleophilic, active hydrogen-containing compound, acting as a donor, to the activated unsaturated group, which serves as an acceptor. When these active hydrogen-containing compounds are C-H compounds such as malonic ester or acetoacetate, the reaction is known as the Michael addition reaction. It is also known that SH- compounds may function as active hydrogen-containing compounds in a reaction mechanism which is similar to the Michael addition reaction. Hereinafter, such a reaction mechanism with SH-compounds is called a thio-Michael reaction.

A composition such as described in the opening paragraph, which is curable by such a thio-Michael reaction, is known from European patent application EP-A 0 160 824. Catalysts mentioned in this disclosure are quaternary ammonium compounds, tetramethyl guanidine, diaza-bicyclo-undecene, and diaza-bicyclo-nonene. Thio-Michael reactions catalysed by these strong bases are hard to control. Such reactions take place either much too fast or not at all, depending on the concentration of the used catalyst. Tertiary amines may be present but, according to this publication, are not reactive at ambient temperatures. Furthermore, the base-catalysed reaction may suffer from acid inhibition.

Carbon dioxide present in the air or an acidic substrate may severely retard or even stop cross-linking.

US 2,759,913 discloses a copolymerisation process of unsaturated monomers
5 with mercapto-functional compounds with a basic catalyst such as trimethyl
benzyl ammonium hydroxide. As mentioned above, reactions with such a
catalyst are hard to control.

British patent application GB-A 2,166,749 discloses a room temperature curable
10 coating composition comprising an unsaturated polyester and a compound
comprising at least three thiol groups and a catalyst which is a tertiary amine,
such as triethyl amine. However, as can be seen from the Examples in GB-A
2,166,749, this reaction takes about 16 hours to cure at ambient temperatures.
Faster reaction will only take place at high temperatures.

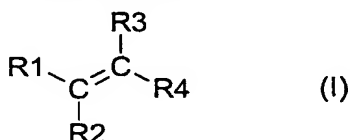
15 The object of the invention is to provide a composition which overcomes the
above-mentioned drawbacks.

The object of the invention is achieved with a composition of the type described
20 in the opening paragraph comprising a catalyst comprising at least one,
optionally blocked, NH-group.

Surprisingly, it has been found that although the prior art teaches that strong
basic catalysts are needed, thio-Michael curable compositions comprising a
25 catalyst according to the invention show rapid curing at ambient temperatures.
This has the evident advantage that short production times are possible. Energy
costs can be saved since curing takes place at ambient temperatures.
Furthermore, in comparison with Michael and thio-Michael reactions catalysed
by strong bases, the reaction time is much less dependent on the amount of
30 catalyst. This is advantageous for ease of formulation. It has also been found
that the process can be carried out with low viscous oligomers. This has the
advantage that compositions can be prepared which contain few if any solvents

but are still sprayable. The reactive groups involved in the curing reaction are much less toxic than most cross-linkable reactive groups in other adhesives or coating compositions, such as isocyanates. After curing, the applied layer is resistant to hydrolysis and degradation. Also, the thermal stability of the sulphide bond is high.

In the compound comprising two or more olefinically unsaturated groups, the olefinically unsaturated groups comprise at least one electron-withdrawing functionality linked to a carbon atom of the unsaturated bond. The olefinically unsaturated bond may be a double or a triple bond. Preferably, the olefinically unsaturated groups of the compound comprising two or more olefinically unsaturated groups have a structure according to the following formula I:



wherein at least one of R1, R2, R3, and R4 comprises an electron-withdrawing functionality linked to a carbon atom of the unsaturated bond and at least one of R1, R2, R3, and R4 is linked to a polyvalent group comprising at least two valencies.

Examples of the electron-withdrawing functionality include carbonyl, carboxyl, ester, thiocarbonyl, thiocarboxyl, thioesters, sulfoxide, sulfonyl, sulfo, phosphate, phosphite, phosphonite, phosphinite, nitro, nitrile, and amide.

In the case of R1, R2, R3, and/or R4 being monovalent, the electron-withdrawing functionality may be attached to a hydrogen atom, linear or branched alkyl, cycloalkyl, alkenyl, cyclo-alkenyl, alkynyl, cyclo-alkynyl, and aryl which may optionally be substituted with various other functionalities, such as carboxylic acid or hydroxide. If they do not comprise an electron-withdrawing functionality, R1, R2, R3, and/or R4 may be independently selected from a hydrogen atom, linear or branched alkyl, cycloalkyl, alkenyl, cyclo-alkenyl,

alkynyl, cyclo-alkynyl, and aryl which may optionally be substituted with various functionalities, such as carboxylic acid or hydroxide. When at least one of R1, R2, R3, and R4 is linked to a polyvalent group and it is not an electron-withdrawing functionality, it may be a simple bond. The polyvalent group links at least two groups according to formula I. The polyvalent group may be selected from a simple bond, substituted or unsubstituted alkylene, cycloalkylene, alkenylene, cycloalkenylene, alkynylene, cycloalkynylene, arylene, or combinations thereof. The polyvalent group may optionally comprise hetero atoms such as -O-, -S-, -Si-, and -P-, and groups such as amide, urea, and ester groups.

Preferably, the group according to formula I is derived from an unsaturated carboxylic acid comprising 2 to 10, preferably 3 to 6, carbon atoms. The carboxylic acid may be mono- or polyunsaturated and may be a monocarboxylic or polycarboxylic acid. Examples of suitable monocarboxylic acids are acrylic acid, methacrylic acid, cinnamic acid, propargylic acid, and dehydrolevulinic acid. Examples of suitable polycarboxylic acids are citraconic acid, maleic acid, itaconic acid, or the anhydrides thereof, and mesaconic acid and fumaric acid. Also monoesters of mono- and polycarboxylic acids and diesters of polycarboxylic acids may be used such as acrylic acid esters, maleic acid mononitrile-monoesters, diethyl maleate, cyanoacrylic acid esters, and alkylidene malonic acid esters as disclosed in WO 98/41561. Acrylic acid or its ester, maleic acid, its ester or anhydride are preferred.

When the group according to formula I is derived from acrylic acid or its ester, a suitable example of a compound comprising two or more olefinically unsaturated groups includes trimethylol propane triacrylate.

When the group according to formula I is derived from maleic acid, ester(s) or anhydride, suitable examples of compounds comprising two or more olefinically unsaturated groups include polyesters of diethyl maleate with diols, such as 1,5-pentane diol, 1,3-propane diol and/or 2-butyl-2-ethyl propane diol, optionally

reacted with polyisocyanates; the reaction product of an epoxy-functional compound, such as Cardura[®] E10 (an aliphatic epoxy compound available from Shell Chemical Company), and isobutyl monomaleate, further reacted with the trimer of isophorone diisocyanate, e.g., Vestanat[®] T1890 E, available from Hüls;
5 and the reaction product of maleic anhydride, dipentaerythritol, and butanol.

Alternatively, the group according to formula I may be derived from unsaturated aldehyde.

- 10 Finally, the compound comprising two or more olefinically unsaturated groups comprising at least one electron-withdrawing functionality linked to a carbon atom of the unsaturated bond may be an unsaturated ketone, such as divinyl ketone or dibenzal acetone.
- 15 The compound comprising at least two mercapto-functional groups may be prepared by direct esterification of a mercapto-functional organic acid with a polyol. Examples of mercapto-functional organic acids include 3-mercaptopropionic acid, 2-mercaptopropionic acid, thio-salicylic acid, mercaptosuccinic acid, mercaptoacetic acid, or cysteine. Examples of
20 compounds prepared according to such a method include pentaerythritol tetrakis (3-mercaptopropionate), pentaerythritol tetrakis (2-mercaptoacetate), trimethylol propane tris (3-mercaptopropionate), trimethylol propane tris (2-mercaptopropionate), and trimethylol propane tris (2-mercaptoacetate). A further example of a compound prepared according to such a method consists
25 of a hyperbranched polyol core based on a starter polyol, e.g. trimethylol propane, and dimethylol propionic acid. This polyol is subsequently esterified with 3-mercaptopropionic acid and isononanoic acid. These methods are described in European patent application EP-A 0 448 224 and international patent application WO 93/17060. Another example of a compound comprising
30 at least two mercapto-functional groups is a mercaptane functional polyurethane resin. In a first step, an isocyanate functional polyurethane is prepared from diols, diisocyanates, and building blocks containing groups which

facilitate the stabilization of the resin in an aqueous dispersion. Such groups are for example polyethylene oxide derivatives, sodium sulfonate groups, and other ionic stabilizing groups. In a second step, the isocyanate functional polyurethane is reacted with di-, tri-, or tetra functional thiols, such as trimethylolpropane trimercapto propionate and pentaerythritol tetramercapto propionate. The equivalent ratio of thiol groups to isocyanate groups in this step is between 2-5:1. Such a resin is suitable for waterborne coating composition.

Alternatively, the compound comprising at least two mercapto-functional groups may for example have a structure according to the following formula: $T[(C_3H_6O)_nCH_2CHOHCH_2SH]_3$, with T being a triol such as trimethylolpropane or glycerol. An example of such a compound is commercially available from Henkel under the trademark Henkel Capcure® 3/800.

Other syntheses to prepare compounds comprising at least two mercapto-functional groups involve:

- the reaction of an aryl or alkyl halide with NaHS to introduce a pendant mercapto group into the alkyl and aryl compounds, respectively;
- the reaction of a Grignard reagent with sulphur to introduce a pendant mercapto group into the structure;
- the reaction of a polymercaptan with a polyolefin according to a nucleophilic reaction, such as a Michael addition reaction, an electrophilic reaction or a radical reaction;
- the reduction of disulphides; and
- other routes, as mentioned in Advanced Organic Chemistry by Jerry March, 4th edition, 1992, page 1298.

It is preferred that the mercapto-functional groups and the olefinically unsaturated groups are present in the composition in an equivalent ratio between 1:2 and 2:1, preferably about 1:1.

In an alternative embodiment of the present invention, the compound comprising two or more olefinically unsaturated groups comprising at least one electron-withdrawing functionality linked to a carbon atom of the unsaturated bond and the compound comprising at least two mercapto-functional groups may be one and the same compound. This embodiment results in a self-cross-linkable composition in the presence of a catalyst comprising at least one, optionally blocked, NH-group.

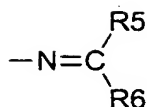
The composition of the present invention comprises a catalyst comprising at least one NH-group which may optionally be blocked. Catalysts comprising at least one NH-group are for example primary and secondary amines. Catalysts comprising at least one blocked NH-group are for example aldimines, ketimines, enamines, and oxazolidines. Also included are catalysts wherein a NH-group originates by daylight or UV radiation.

Examples of primary amines include isophorone diamine, butyl amine, n-octyl amine, n-nonyl amine, N,N-diethylamine-propyl-3-amine, 4-(aminomethyl)-1,8-octane diamine, aniline, methoxy aniline, carboxy ethyl aniline, phenylene diamine, and mixtures thereof. Also included are polyoxyalkylene amines, such as polyoxy ethylene/polyoxy propylene mono-, di, or triamines. These are available from Huntsman under the tradename Jeffamine®, such as Jeffamine® T-403.

A suitable secondary amine is for instance di-octyl amine.

Other suitable catalysts are ketimines, i.e. the condensation products of primary amino groups with ketones, or aldimines, i.e. the condensation products of primary amino groups with aldehydes. In these condensation reactions, groups with the following formula are formed:

8



wherein R5 is an alkyl group, a cyclic group, or an aromatic group, and R6 is hydrogen in the case of an aldimine or an alkyl group, a cyclic group, or an aromatic group in the case of a ketimine. Preferably, R5 and/or R6 are alkyl groups. More preferably, R5 and/or R6 are alkyl groups comprising 1 – 10 carbon atoms.

Examples of aldimines include the condensation products of monofunctional amines like n-octyl- or n-nonyl amine and polyfunctional amines like isophorone diamine with acetaldehyde, propionaldehyde, isobutyraldehyde, n-octyl aldehyde, 2-ethylhexyl aldehyde, or n-nonyl aldehyde. A commercial product is for example Vestamine® A139, isophorone bisisobutyraldimine, ex Hüls. Also aromatic aldehydes and dialdehydes and heterocyclic aldehydes and dialdehydes and mixtures thereof may be used. Examples of aromatic aldehydes include 4-acetamidobenzaldehyde, anthracene-9-carboxaldehyde, 3-benzyloxybenzaldehyde, 4-benzyloxybenzaldehyde, 3-benzyloxy-4-methoxybenzaldehyde, 3,5-bis(trifluoromethyl) benzaldehyde, 3-bromo-4-methoxybenzaldehyde, 5-bromo-2-methoxybenzaldehyde, 2-bromobenzaldehyde, 3-bromobenzaldehyde, 4-bromobenzaldehyde, α-bromocinnamaldehyde, 3-bromo-4-fluorobenzaldehyde, 4-bromo-2-fluorobenzaldehyde, 5-bromo-2-fluorobenzaldehyde, 5-bromo-2-hydroxybenzaldehyde, 2-chlorobenzaldehyde, 3-chlorobenzaldehyde, 4-chlorobenzaldehyde, and other halogen substituted aromatic aldehydes, 4-butoxybenzaldehyde, 2,3-dihydroxybenzaldehyde and other isomers, 2,3-dimethoxybenzaldehyde and other isomers, 3,4-dimethoxy-6-nitrobenzaldehyde, 4-dimethylaminobenzaldehyde, 2,5-dimethyl-p-anisaldehyde, 2,4-dinitrobenzaldehyde, 4-phenoxybenzaldehyde, 3-phenoxybenzaldehyde, 4-phenylbenzaldehyde, p-tolualdehyde, o-tolualdehyde, and m-tolualdehyde, 2,4,6-trimethylbenzaldehyde and other alkyl substituted

- benzaldehydes. Examples of aromatic dialdehydes include 1,3-benzenedialdehyde and terephthalaldehyde. Examples of heterocyclic aldehydes include thiophene-2-carboxaldehyde, thiophene-3-carboxaldehyde, 5-acetoxymethyl-2-furaldehyde, 4-bromo-2-thiophenecarboxaldehyde, 3,5-dimethyl-1-phenylpyrazole-4-carboxaldehyde, 3-phenyl-1h-pyrazole-4-carboxaldehyde, picolinaldehyde, 4-pyridinecarboxaldehyde, 3-pyridinecarboxaldehyde, and 4-quinolinecarboxaldehyde. An example of a heterocyclic dialdehyde includes 2,5-thiophenedicarboxaldehyde.
- 10 Suitable ketimines are the condensation products of mono- and polyfunctional amines with for instance acetone, methylethyl ketone, methylisobutyl ketone, methylisoamyl ketone, ethylamyl ketone, cyclohexanone, acetophenone, hydroxyacetophenone, or acetyl biphenyl. One example is the reaction product of 3 moles of ethyl amyl ketone and 4-(aminomethyl)-1,8-octane diamine.
- 15 An example of a suitable oxazolidine is Incozol[®] LV, available from Industrial Copolymers Ltd., i.e. the reaction product of 1 mole of diallyl carbonate and 2 moles of an oxazolidine produced from diethanolamine and isobutyraldehyde.
- 20 An example of a suitable enamine is 1-pyrrolidino-1-cyclohexene.
- Catalysts wherein an NH-group originates by UV radiation are disclosed by J.F. Cameron et al., J. Org. Chem., 1990, 55, pp. 5919-5922. Examples of catalysts wherein an NH-group originates by UV radiation include N-[[1-(3,5-dimethoxyphenyl)-1-methyl-ethoxy] carbonyl] cyclohexylamine, N,N'-bis[[1-(3,5-dimethoxyphenyl)-1-methylethoxy] carbonyl] hexane-1,6-diamine, N-[[1-(3,5-dimethoxyphenyl)-1-methylethoxy] carbonyl] piperidine, [[1-(3,5-dimethoxyphenyl)-1-methylethoxy] carbonyl] amine, [[[2,6-dinitrobenzyl)oxy] carbonyl] cyclohexyl amine, 4,4'-[bis[[2-nitrobenzyl)oxy] carbonyl] trimethylene dipiperidine, 3,3',5,5'-tetramethoxybenzoin cyclohexyl carbamate, and mixtures thereof.
- 25
- 30

The NH-functional catalysts, optionally blocked, can be used alone, as mixtures of catalysts of the same nature, or as mixtures of catalysts of a different nature. In particular, if the composition according to the invention is used as a primer, it is preferred to use a mixture of aldimines and ketimines as a catalyst. A mixing weight ratio of 0,1-10:1, preferably 2-6:1, can be used. It has been found that this results in a better adhesion to the substrate.

Since the reaction time is only dependent on the amount of catalyst to a small extent, high concentrations of catalyst can be used without making the reaction uncontrollable. It has been found that the sensitivity of a base coat or top coat to an acidic substrate or primer, and hence the curing time, is lower when higher concentrations of catalysts according to the invention are used. This sensitivity is believed to be reduced even more if tertiary amines are added to the top coat or base coat composition, since they are believed to adhere to the used acidic primer or acidic substrate and to neutralise its acidity. The full amount of catalyst is then used to catalyse the reaction. A suitable tertiary amine is N,N-dimethyl-ethanol-amine.

Preferably, the catalyst is used in an amount of 0,01 - 10 eq.% nitrogen groups, based on the total of unsaturated and thiol groups. An amount of 0,1-6 eq.% is more preferred.

The composition according to the present invention may be a water-borne composition, a solvent-borne composition or a solvent-free composition. Since the composition may be composed of low viscous oligomers, it is especially suitable for use as a high-solids coating or a solvent-free coating. Preferably, the theoretical volatile organic content (VOC) of the composition is less than 450 g/l, more preferably less than 350 g/l, most preferably less than 250 g/l.

In order to further reduce the volatile organic content, reactive diluents may be used, such as diethyl maleate, methoxypropyl citraconimide, diethylbenzylidene malonate, an α,β -unsaturated aldehyde, e.g., cinnamaldehyde or citral, and

monothiol functional compounds, such as dodecyl mercaptane and mercapto functional silanes, such as γ -mercapto-propyl-trimethoxysilane. The mercapto-functional groups and the olefinically unsaturated groups of the reactive diluents are also taken into account with regard to the above-mentioned equivalent ratio.

5

The present compositions are of particular interest in coating compositions or adhesives. Preferably, a two-pack composition is used. Preferably, the first component of the two-pack coating or adhesive comprises the compound comprising two or more olefinically unsaturated groups as well as the
10 compound comprising at least two mercapto-functional groups, while the second component of the composition comprises a small amount of a catalyst solution. However, if so desired, the second component may comprise, next to the catalyst, a part or the total amount of either the compound comprising olefinically unsaturated groups or the compound comprising mercapto-
15 functional groups.

The formulations may contain pigments, effect pigments, such as aluminium parts, UV absorbers, adhesion promoters, such as epoxy silane, HALS-type stabilizers, flow additives or other additives.

20

The composition according to the present invention can be applied by conventional methods, including spraying, brushing, roller coating or dipping. However, the composition of the present invention is particularly suitable for application by an external mixing apparatus, one wherein a liquid composition
25 comprising:

- a compound comprising two or more olefinically unsaturated groups comprising at least one electron-withdrawing functionality linked to a carbon atom of the unsaturated group, and
 - a compound comprising at least two mercapto-functional groups,
30. is sprayed via a spray nozzle, with a small amount of a liquid catalyst composition comprising at least one catalyst comprising at least one, optionally blocked, NH group, being injected into the spray of the sprayed composition.

Such an apparatus is described, for example, in WO 98/41316. Due to the very effective use of the catalysts, the compositions according to the present invention have very short curing times, which makes this method specifically suitable for these compositions.

5

The composition according to the invention can be used on various substrates, in particular wood, plastics, and metal substrates such as aluminium, steel, or galvanised steel, for industrial applications of any kind. The composition can be used for instance as an adhesive or as a coating, e.g., as a putty, primer, filler,
10 base coat, top coat or clear coat. The composition is particularly advantageous for use as a coating for car repair, since it is easily sprayable and can be applied at ambient temperatures. Generally in car repair, several layers need to be applied, such as a primer, a base coat, and a clear coat. Because of the short drying times, a next layer can be applied within a short time from applying
15 a first layer.

The invention is further illustrated by the following examples.

EXAMPLES

In the following Examples the compounds listed below are available as indicated.

5

Compounds	Description	Available from
Autobase [®]	solvent-borne base coat	Akzo Nobel Car Refinishes
Autocryl [®] 3110	filler	Akzo Nobel Car Refinishes
Autocryl [®] LV	solvent-borne top coat	Akzo Nobel Car Refinishes
Autowave [®]	waterborne base coat	Akzo Nobel Car Refinishes
Byk [®] 306	substrate wetting additive	BYK-Chemie
Byk [®] 333	silicon flow additive	BYK-Chemie
Cardura [®] E10	aliphatic epoxy compound	Shell Chemical Company
Disperbyk [®] 110	dispersing agent	BYK-Chemie
Incozol [®] LV	oxazolidine	Industrial Copolymers Ltd
Jeffamine [®] T 403	primary triamino-functional polyalkylene oxide	Huntsman Corporation
Sparkle Silver [®] E 5000 AR	non-leafing aluminium paste	Silberline Ltd
Tinuvin [®] 1130	UV absorber	Ciba
Tinuvin [®] 123	sterically hindered amine light stabiliser	Ciba
Tinuvin [®] 292	sterically hindered amine light stabiliser	Ciba
Vestamine [®] A139	isophorone bisisobutyraldimine	Hüls
Vestanat [®] T1890 E	trimer of isophorone diisocyanate	Hüls
Washprimer [®] CR	primer	Akzo Nobel Car Refinishes

In the Examples, the following abbreviations are used for the compounds as indicated.

- 10 DBU diazabicycloundecene
DMEA N,N-dimethyl-ethanol-amine
IPDA isophorone diamine
PTMP pentaerythritol tetrakis(3-mercaptopropionate)

- TAN-EAK the reaction product of 3 moles of ethyl amyl ketone and 4-(aminomethyl)-1,8-octane diamine
- TMP(2MA)3 trimethylol propane tris (2-mercaptoacetate)
- TMP(3MPA)3 trimethylol propane tris (3-mercaptopropionate)
- 5 TMPTA trimethylol propane triacrylate

In the Examples, mercapto-functional groups and olefinically unsaturated groups are present in the coating compositions in an equivalent ratio of 1:1.

- 10 Curing times were measured using a BK drying recorder. The curing time is the time between the application of the sample and the phase when the pen of the BK drying recorder does not damage the coating down to the substrate anymore (phase III).
- 15 A coating is free to handle when the mark from firm pushing with the thumb disappears after 1 or 2 minutes.

Viscosity is measured with a Cone and Plate viscometer, type CAP 2000.

- 20 Adhesion was tested using the so called pull-off test, in which a cross-cut at 45° is made with an Olfa® cutter, after which a standard type adhesion tape is stuck on the paint and gently pulled off again. The values 1 – 10 represent a scale for evaluation of the adhesion ranging from very poor adhesion (1) to excellent adhesion (10).

25

Gitterschnitt adhesion was measured in accordance with ISO 2409. The adhesion is determined visually on a scale from 0 (=no detachment) to 5 (=total detachment). The condense test used together with the Gitterschnitt adhesion test had the following conditions: 10 days at 100% relative humidity at 42°C.

30

Stone chip resistance was measured according to the Ford standard test Ford 57-4. The values 0-7 represent a scale for evaluation of the stone chip resistance ranging from very poor (7) to excellent (0).

- 5 The accelerated weathering test was carried out in accordance with international standard ISO 2810.

The presence of blisters in cured layers was tested in accordance with ASTM-D714. The results are scaled in values ranging from 1 (big blisters) to 10 (no blisters), with a further code for the blister density, F standing for "few," M for "medium," and D for "dense."

Example 1: Preparation of a maleate-functional polyester

- 15 A 2-litre 4-neck flask was fitted with a variable speed stirrer, thermocouples in combination with a controller, a distillation column, a condenser, a nitrogen sparge, and a heating mantle. The flask was charged with 1240 grams of diethyl maleate, 235 grams of 1,5-pentane diol, 360 grams of 2-butyl-2-ethyl propane diol, 3,7 grams of dibutyl tin oxide catalyst, and 5 wt.% of xylene. The nitrogen
20 sparge and the stirrer were turned on. The heating mantle was set to heat the reactor charge to 150°C with a limit of 79°C at the top of the column. Ethanol was collected and when the distillation rate diminished, another amount of 5 wt.% xylene was added in about 60 minutes, followed by reaction under diminished pressure. At the end the amount of xylene, together with the ethanol
25 residue was distilled off. The reaction conversion, calculated from the amount of ethanol, was more than 98%. The solids content of the end product was 99,6%. The viscosity at 23°C was 1 Pa.s. The maleate number was 278 mg KOH/g solids.

Example 2: Preparation of a maleate-functional oligo-urethane

A 2-litre 4-neck flask was fitted with a variable speed stirrer, thermocouples in combination with a controller, a reflux condenser, a nitrogen sparge, and a heating mantle. The flask was charged with 375 grams of Cardura® E10. The nitrogen sparge and the stirrer were turned on and the batch charge was heated to a temperature of 100° C. Next, 260 grams of isobutyl monomaleate and 0,64 gram of chromium(III) 2-ethyl hexanoate were added while the batch temperature was kept at 120°C (exothermic reaction). The reaction was carried out at 120°C until the COOH-conversion was at least 98%, followed by cooling down to 80°C. Then, 0,5 gram of dibutyl tin dilaurate catalyst was added, followed by the addition of 525 grams of Vestanat® T1890 E, while the batch temperature was kept below 90°C. The reaction was completed at 90°C when an NCO conversion of at least 98% was reached. The product was cooled down, diluted with n-butyl acetate to a solids content of 70 wt.%. The measured solids content of the resulting product was 72,4%. The viscosity at 23°C was 1,9 Pa.s. The maleate number was 84 mg KOH/g solids.

Example 3: Preparation of a mercapto-functional polyester

A 2-litre 5-neck flask was fitted with a variable speed stirrer, thermocouples in combination with a controller, a Vigreux column, a condenser, a nitrogen sparge, and a heating mantle. The flask was charged with 48 grams of trimethylol propane, 763 grams of dimethylol propionic acid, and, as a catalyst, 20,5 grams of para-toluene sulfonic acid. The nitrogen sparge and the heating mantle were turned on. The stirrer was turned on when the batch charge had been melted. The first step of the esterification at 140°C was carried out until an acid value of less than 10 mg KOH/g solids was reached. Next, 108 grams of isononanoic acid were added, followed by rinsing with about 5 wt.% of xylene. During the same time the batch solution was cooled down to 120°C. Next, 582 grams of 3-mercaptopropionic acid were added in about 60 minutes, followed

by rinsing with 5 wt.% of xylene. During the addition of the 3-mercaptopropionic acid the batch temperature was increased to 140°C. The second step of the esterification was carried out at 140°C, with an additional 10 grams of para-toluene sulfonic acid, with xylene refluxing under diminished pressure, until an acid value of less than 15 mg KOH/g solids was reached. Then, 6 grams of lithium carbonate were added, followed by cooling down and diluting with n-butyl acetate with a dilution to solids content of 81 wt.%. The preparation was completed by filtration at about 70°C using a pressure filter with filter aid, which yielded a clear resin. The total OH- and SH-value of the resulting product was 254 mg KOH/g solids. The solids content was 81,8%. The viscosity at 23°C was 1,3 Pa.s.

Examples 4 – 11, Comparative Examples A and B

In the following Examples 4 – 11 and Comparative Examples A and B, a coating composition was prepared comprising 40 g of PTMP and 36 g of TMPTA. Different catalysts were used, as is shown in the following Table I. In Examples 4 – 11 a catalyst according to the invention was used. In Comparative Examples A and B prior art catalysts were used. In all of the Examples 4 – 11 and Comparative Examples A and B, 0,5 eq.% of catalyst was used. The compositions were prepared and subsequently applied on a glass plate using a 200-micron draw bar. The samples were cured at a temperature of 21°C.

Table I

Ex.	Catalyst	Curing Time
4	IPDA	<1 minute
5	1-N,N-diethylaminopropyl-3-amine	1 minute
6	Dioctyl amine	2 minutes
7	IPDA bis nonyl aldimine	12 minutes
8	TAN-EAK	5 minutes
9	1-Pyrrolidino 1-cyclohexene	8 minutes
10	Vestamine® A139	12 minutes
11	Incozol® LV	105 minutes
A	Triethylamine	> 24 hours
B	Sodium ethanolate	> 24 hours

In Examples 4 – 11 and Comparative Examples A and B, the theoretical VOC was 165 g/l.

5

Comparative Examples A and B illustrate that tertiary amine and sodium ethanolate catalysts are not highly effective at room temperature in comparison with the catalysts according to the invention in equal concentration. Examples 4 - 11 show the relative effectiveness of different catalysts according to the invention. Curing times are much shorter than the curing times in Comparative Examples A and B.

10

Examples 12 - 14

15

Example 10 was repeated, except that different amounts of catalyst, i.e. Vestamine® A139, was used. The equimolar amount of catalyst in Example 10 corresponds to 2 wt.%. The corresponding test results, as shown in Table II, indicate the sensitivity of the system to the amount of catalyst used.

Table II

Example	Catalyst	Amount	Curing Time
12	Vestamine [®] A139	0,5 wt.%	22 minutes
13	Vestamine [®] A139	1 wt.%	15 minutes
10	Vestamine [®] A139	2 wt.%	12 minutes
14	Vestamine [®] A139	3 wt.%	10 minutes

In these Examples, the theoretical VOC was 165 g/l.

5 Comparative Examples C and D

Comparative Example A was repeated, except that another catalyst, i.e. DBU, was used in two different amounts. The test results as shown in Table III show that the use of DBU as a catalyst either results in an extremely fast reaction with a relatively small catalyst concentration, or does not result in cross-linking at all when the concentration is lowered somewhat. The same occurs with other strong basic catalysts.

Table III

Comp. Example	Catalyst	Amount	Curing Time
C	DBU	0,2 wt.%	<< 1 minute
D	DBU	0,1 wt.%	> 24 hours

In these Comparative Examples, the theoretical VOC was 165 g/l.

Example 15

A coating composition comprised 40 g PTMP and 64,8 g of the maleate-functional polyester of Example 1. The used catalyst was 2 wt.% Vestamine[®] A139 (2,3 eq.%). The theoretical VOC was 400 g/l. Application was carried out according to Example 4. The curing time was 22 minutes at 21°C.

Example 16 and Comparative Example E

In Example 16 and corresponding Comparative Example E, 31,2 g of PTMP were used in combination with 50 g of the maleate-functional polyester as prepared in Example 1. In Example 16, 1,5 wt.% of Vestamine® A139 was used as a catalyst (1,7 eq.%). In Comparative Example E, DMEA was used as the catalyst in an amount equimolar to the amount of catalyst in Example 16. The theoretical VOC was 250 g/l for both Example 16 and Comparative Example E. The composition was applied on a substrate in the same way as in Example 4.

The curing time for Example 16 was 20 minutes, while the curing time for Comparative Example E was longer than 24 hours at 21°C.

Examples 17, 18, 19, and Comparative Example F

The following primer/ filler formulation was prepared:

	mercapto-functional polyester of Example 3	15,21 grams
	Disperbyk® 110	0,40 gram
	butyl acetate	6,26 grams
20	calcium carbonate	14,20 grams
	magnesium silicate	5,70 grams
	titanium dioxide	14,00 grams
	zinc orthophosphate	6,30 grams
	low colour furnace black	0,04 gram
25	maleate-functional polyester of Example 1	13,80 grams

In order to give the composition the desired viscosity suitable for spraying, another 10,00 grams of butyl acetate were added.

This primer/filler formulation was applied by spraying with an external mixing apparatus using different catalysts on a steel substrate, the thickness of the coating layer being 80 µ after curing at 21°C. In Example 17, 2,5 eq.% TAN-

EAK was used. The filler was sandable after 5 minutes. In Example 18, 2,5 eq.% IPDA was used. The filler was sandable after 30 minutes.

In Example 17 as well as in Example 18 the theoretical VOC was 290 g/l.

5

The composition as prepared in Example 18 was applied by spraying with an external mixing apparatus on a steel substrate. In Comparative Example F, Autocryl® 3110 filler was applied on a steel substrate. Subsequently, all primed substrates were treated with a top coat, Autocryl® LV. Curing took place at a temperature of 23°C for several days. The samples were then immersed in water for several days, after which the cross-cut adhesion of the primer to the steel substrate was evaluated. The results are given in Table IV.

To the composition prepared in Example 18 was added an adhesion promoter, namely 4% by weight of solid binder of epoxy silane (Example 19). The same tests were carried out as mentioned above. The results are also given in Table IV.

Table IV – primer / steel adhesion

Water immersion (days):	0	1	7	14	Recovery	Blisters
C. Ex. F	8	8	8	8	9	9F
Ex. 18	9	1	-	-	9	9F
Ex. 19	9	10	9	9	9	9F

20

For the following tests, samples were used of the compositions of Example 18 and Comparative Example F. These primer samples were applied on substrates that had been pre-treated with Washprimer® CR. Subsequently, a top coat, Autocryl® LV, was applied over the primers. Curing took place at 21°C. The results are given in the following table V.

25

Table V

	Stone chip resistance		Gitterschnitt adhesion		Accelerated weathering
Sample	Before soak	After soak	Before condense test	After condense test	Adhesion loss in mm
Ex. 18	3	6	0-1	1	1,5
C. Ex. F	3	6	0-1	1	1

Example 20

5

In this Example, a base coat was prepared according to the present invention.

	PTMP	60,00 grams
	maleate-functional polyester of Example 1	97,41 grams
10	Sparkle Silver® E 5000 AR	48,43 grams
	butyl acetate	69,58 grams

The theoretical VOC was 165 g/l. This base coat formulation was spray-applied on a steel substrate precoated with Autocryl® 3110 filler. The base coat was applied with the external mixing apparatus described *supra* using 2,5 eq.% TAN-EAK. The resulting film was over-sprayable after 7 minutes of curing at 21°C.

15

Example 21

20

A clear coat comprising the following compounds was formulated:

	PTMP	120,00 grams
	TMPTA	96,90 grams
25	butylacetate	36,00 grams

23

Byk® 306	0,85 gram
Tinuvin® 292	1,08 grams
Tinuvin® 1130	2,17 grams

- 5 The theoretical VOC was 435 g/l. This formulation was sprayed with an external mixing apparatus with 5 eq.% catalyst solution of TAN-EAK. The layer thickness was 50 μ after curing. It was free to handle after 10 minutes curing at room temperature when spray-applied on various commercial base coats, such as Autobase® and Autowave®.

10

Example 22

Another clear coat was prepared with the following formulation:

15	PTMP	13,24 grams
	maleate-functional oligo-urethane of Example 2	100,00 grams
	butyl acetate	44,94 grams
	Tinuvin® 123	0,48 gram
	Tinuvin® 1130	0,48 gram
20	Byk® 333	0,27 gram

This formulation was cross-linked with 5 eq.% catalyst solution of Vestamine® A139 and applied, cured, and tested as in Example 21. This clear coat formulation was free to handle after 20 minutes curing at room temperature.

25

Example 23

A putty was formulated comprising a maleate-functional paste, a mercapto-functional paste, and a catalyst.

30

The maleate-functional paste comprised:

titanium dioxide	5,7 grams
------------------	-----------

24

barium sulphate	12,1 grams
magnesium silicate	82,2 grams
maleate-functional polyester of Example 1	100,0 grams

5 The mercapto-functional paste comprised:

titanium dioxide	2,8 grams
barium sulphate	6,1 grams
magnesium silicate	41,1 grams
PTMP	23,5 grams

10

The used catalyst was 1,8 grams of TAN-EAK (2,75 eq.%). When mixing the above two pastes and the catalyst, a putty with a workability time of 3,5 minutes was obtained which was solid after 4,5 minutes and sandable after 10 minutes, after application on a steel substrate and curing at 21°C.

15

Example 24

The same composition was made as in Example 23, except that the catalyst was replaced by Vestamine® A139 (2,75 eq.%). A putty with a workability time of 5,5 minutes was obtained which was solid after 41 minutes and sandable after more than one hour, after application on a steel substrate and curing at 21°C.

20

Examples 25 and 26

25

In Examples 25 and 26 two water based clear coats according to the invention were made.

30

An acryloyl-functional polyurethane emulsion (43% s.c. in water, 454 C=C equivalent by weight on solid) was mixed with TMP(3MPA)3 (60% s.c. in methoxy propyl acetate). In Example 25, this composition was cured by IPDA (5

eq.%), while in Example 26, the composition was cured by Jeffamine® T 403 (2,7 eq.%).

The clear coats were applied on a glass substrate using a 100-micron draw bar
5 and cured at 21°C.

Table VI

	Example 25	Example 26
acryloyl-functional polyurethane emulsion	31,8 grams	31,8 grams
TMP(3MPA)3	6,7 grams	6,7 grams
IPDA	0,28 gram	-
Jeffamine® T 403	-	0,24 gram
Curing time	24 minutes	32 minutes

10 Examples 27 – 35

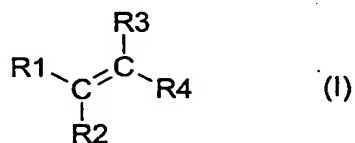
In the following Examples 27 - 35, coating compositions were prepared comprising the maleate-functional polyester of Example 1 and different mercapto functional compounds in an equivalent ratio of mercapto-functional
15 groups and olefinically unsaturated groups of 1:1. Different catalysts were used in an amount of 0,75 eq.%. The compositions were applied on a glass plate using a 200-micron draw bar. The samples were cured at a temperature of 21°C. Table VII lists the curing times in minutes.

Table VII

Ex.		Incozol LV
27	PTMP	90
28	TMP(3MPA)3	94,8
29	TMP(2MA)3	21,3
		Vestamine A139
30	PTMP	20,4
31	TMP(3MPA)3	33,8
32	TMP(2MA)3	29,7
		TAN/ EAK
33	PTMP	5,2
34	TMP(3MPA)3	5,6
35	TMP(2MA)3	<1

CLAIMS

1. Composition comprising
 - a compound comprising two or more olefinically unsaturated groups comprising at least one electron-withdrawing functionality linked to a carbon atom of the unsaturated bond;
 - a compound comprising at least two mercapto-functional groups; and
 - a catalyst comprising at least one, optionally blocked, NH-group.
2. Composition according to claim 1, characterised in that the catalyst is selected from primary or secondary amines, aldimines, ketimines, enamines, oxazolidines, or mixtures thereof.
3. Composition according to either of the preceding claims, characterised in that the catalyst is used in an amount of 0,01 - 10 eq.% nitrogen groups, based on the total of unsaturated and thiol groups.
4. Composition according to any one of the preceding claims, characterised in that the olefinically unsaturated groups of the compound comprising two or more olefinically unsaturated groups have a structure according to the following formula I:



- wherein at least one of R1, R2, R3, and R4 comprises an electron-withdrawing functionality linked to a carbon atom of the unsaturated bond and at least one of R1, R2, R3, and R4 is linked to a polyvalent group comprising at least two valencies.

5. Composition according to claim 4, characterised in that the electron-withdrawing functionality is selected from carbonyl, carboxyl, ester,

thiocarbonyl, thiocarboxyl, thioesters, sulfoxide, sulfonyl, sulfo, phosphate, phosphite, phosphonite, phosphinite, nitro, nitrile, and amide.

- 5 6. Composition according to claim 5, characterised in that at least one of the groups according to formula I is derived from an unsaturated carboxylic acid comprising 2 to 10 carbon atoms.
- 10 7. Composition according to any one of the preceding claims, characterised in that the mercapto-functional groups and the olefinically unsaturated groups are present in an equivalent ratio between 1:2 and 2:1.
- 15 8. Method for the application of a composition according to any of the preceding claims, characterised in that a liquid composition comprising
 - a compound comprising two or more olefinically unsaturated groups comprising at least one electron-withdrawing functionality linked to a carbon atom of the unsaturated bond; and
 - a compound comprising at least two mercapto-functional groups;is sprayed via a spray nozzle and that a small amount of a liquid catalyst composition comprising at least one catalyst comprising at least one,
20 optionally blocked, NH-group is injected into the spray of the sprayed composition.
- 25 9. Use of the composition according to any one of claims 1 – 7 as a coating composition.
10. Use of the composition according to any one of claims 1 – 7 as an adhesive.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/03746

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G18/67 C08G63/91

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 840 823 A (WUESTEFELD RENATE ET AL) 24 November 1998 (1998-11-24) page 1, column 1, line 32 page 1, column 1, line 5 - line 30 page 3, column 6, line 55 - line 66 page 4, column 7, line 30 - line 40 page 6, column 11, line 20 - line 40; claims 1-9	1-10
A	EP 0 284 374 A (SHOWA DENKO KK) 28 September 1988 (1988-09-28) page 3, line 27 page 5, line 29-35 page 6, line 3 - line 11 -/--	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"S" document member of the same patent family

Date of the actual completion of the international search

7 July 2000

Date of mailing of the international search report

25/07/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Bergmans, K

INTERNATIONAL SEARCH REPORT

Int. l. Application No
PCT/EP 00/03746

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 283 480 A (DAVIES WILLIAM D ET AL) 11 August 1981 (1981-08-11) page 3, column 4, line 25 page 3, column 4, line 30 page 3, column 4, line 56,57 page 3, column 3, line 66 -----	1-10
A	US 4 730 033 A (HORLEY SUSAN M ET AL) 8 March 1988 (1988-03-08) page 1, column 1, line 54 -page 1, column 2, line 62 page 1, column 1, line 35 page 3, column 5, line 9 -page 3, column 6, line 5 -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/03746

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5840823 A	24-11-1998	DE 19608610 A EP 0794204 A JP 10053702 A	11-09-1997 10-09-1997 24-02-1998
EP 0284374 A	28-09-1988	JP 1687663 C JP 3053329 B JP 63235332 A JP 1691584 C JP 3053330 B JP 63238132 A US 5047576 A	11-08-1992 14-08-1991 30-09-1988 27-08-1992 14-08-1991 04-10-1988 10-09-1991
US 4283480 A	11-08-1981	GB 2030584 A AT 7545 T CA 1136796 A DE 2966989 D EP 0009967 A JP 55058226 A	10-04-1980 15-06-1984 30-11-1982 20-06-1984 16-04-1980 30-04-1980
US 4730033 A	08-03-1988	AT 79894 T AU 581468 B AU 4900885 A BR 8505512 A CA 1280533 A DE 3586562 A DE 3586562 T DK 510685 A EP 0184302 A ES 548539 D ES 8705014 A FI 854280 A GB 2166749 A, B GR 852654 A JP 1924414 C JP 6051861 B JP 61113658 A NO 854388 A NZ 213900 A PL 256048 A PT 81426 A, B ZA 8508187 A ZM 8285 A ZW 18685 A	15-09-1992 23-02-1989 15-05-1986 05-08-1986 19-02-1991 01-10-1992 01-07-1993 06-05-1986 11-06-1986 16-04-1987 01-07-1987 06-05-1986 14-05-1986 03-02-1986 25-04-1995 06-07-1994 31-05-1986 06-05-1986 30-06-1988 23-03-1987 01-12-1985 29-04-1987 28-05-1986 20-05-1987